OFFICE OF NAVAL RESEARCH

Contract Nonr-562(03)

NR-051-284

Final Report

DIELECTRIC PROPERTIES OF ALCOHOLS AND GLYCOLS

By

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I. Objectives of the Contract. In the original contract proposal dated 4 April 1951, a program of research on dielectric properties of alcohols and glycols was outlined.

The aim of the work was to obtain definitive measurements of both equilibrium and relaxation behavior over wide ranges of temperature and frequency for representative systems as an aid to better understanding of their constitution and molecular interactions. The specific systems proposed on the basis of work in hand at the time included trimethylene glycol and lower aliphatic alcohols. In the request for extension of the contract for four months to 31 January. 1954, further problems of measuring dielectric relaxation in glycerol as a function of temperature and pressure and development of methods for ultra-high frequency measurements were outlined. During the period of contract support, a considerable body of results on all these problems has been obtained and these have led to better understanding of the underlying factors. As the results have been presented as parts of two technical reports listed in II, they need not be described again here in detail. Some of the earlier work has been published, as listed in IV, and papers in preparation are listed in V.

II. Personnel Associated with the Contract and Their Activities. Robert H. Cole, Project Supervisor, 1951-1954. General supervision of work over contract period, and research in the summer of 1952

and part of the summer of 1953. The latter included research on trimethylene glycol, analysis of dielectric measurements reported as Part II of second technical report, development of ultrahigh frequency methods, and theory of dielectric properties of alcohols in relation to hydrogen bonding. Andrew Gilchrist, Post-doctoral Research Associate, 1953-54. Studied effects of hydrostatic pressures up to 1000 atmospheres on dielectric relaxation in glycerol and began similar measurements for n-propyl alcohol. Experimental work included development of pressure techniques and thermostats for temperatures from 25° C. to -150° C.

F. X. Hassion, Research Assistant, 1951-53. Studied dielectric relaxation in ethyl and isopropyl alcohols.

Walter Dannhauser, Research Assistant, summers of 1952, 1953. Measurements of dielectric constants of trifluoroacetic and acetic acids. Partial studies, dielectric constant and loss in normal and isobutyl alcohols (since completed).

Stephen Havriliak, Research Assistant, summer of 1953. Determination of dielectric constants of solid hydrogen sulfide.

S. E. Lovell, Research Assistant, summer of 1953. Development of methods for measurement of dielectric constant and loss in the range 2 Mc - 250 Mc.

III. Status and Technical Reports.

First Status Report, March 3, 1952.

Second Status Report, October 1, 1952.

First Technical Report, November 16, 1953.

I. Dielectric Properties of Liquid Ethanol and 2-Propanol. F. X. Hassion and R. H. Cole

II. Dielectric Properties of Trimethylene Glycol
R. H. Cole and D. W. Davidson

Second Technical Report, March 15, 1954.

I. Determination of Dielectric Properties under Constant Volume Conditions.
Andrew Gilchrist

II. On the Analysis of Dielectric Relaxation Measurements.
Robert H. Cole

III. Dielectric Constants of Liquid and Solid Hydrogen Sulfide.
Stephen Havriliak, Richard W. Swenson, and Robert H. Cole

IV. Publications.

High Frequency Dispersion in n-Propanol, R. H. Cole & D. W. Davidson, J. Chem. Phys. 20, 1389 (1952).

On the Dielectric Constant of Trifluoroacetic Acid, Walter Dannhauser and R. H. Cole, J. Am. Chem. Soc. 74, 6105 (1952).

Dielectric Relaxation Processes in Ethanol, F. X. Hassion & R. H. Cole, Nature, 172, 212 (1953).

V. Papers in Preparation.

Dielectric Properties of Ethyl & iso-Propyl Alcohols and of Ethyl Alcohol-Water Solutions. (F. X. Hassion & R. H. Cole)

Dielectric Properties of Normal & Iso Butyl Alcohols (W. Dannhauser & R. H. Cole)

On the Analysis of Dielectric Relaxation Measurements (R. H. Cole)

Dielectric Relaxation in Glycerol & n-Propyl Alcohol as a Function of Pressure and Temperature (A. Gilchrist)

Thermostats for Low Temperatures (0°C. to -150°C.) (A. Gilchrist)

Measurement of Dielectric Constant and Loss from 2 Mc to 250 Mc. (L. E. Lovell and R. H. Cole)

VI. Summary. With completion of contract supported and other related research, there now exist quite definitive measurements for six lower alcohols and three three-carbon glycols over ranges of temperature to -150°C. and frequencies from 10 cycles or less to 2 megacycles or higher. Theories of molecular origins of the observed dispersion processes have been advanced and are being developed further. Measurements are in hand and being continued to determine the influence of pressure and hence molar volume on dielectric relaxation. The engineering of adequate methods for studying dielectric relaxation of lossy substances in the range 2 Mc - 250 Mc was begun. Since the termination of contract support this work has been continued to the point that preliminary measurements confirm the validity of the procedures which were devised and partly developed.

The results obtained have, in the supervisor's estimation, considerably extended our knowledge of dielectric behavior and led to conclusions with significant bearing on properties of hydrogen bonding liquids. The work has brought to light and clarified aspects of dielectric behavior previously unknown or misinterpreted. It has also shown both the necessity of sufficiently comprehensive measurements for a proper definition of dielectric behavior and the value of such measurements for a better understanding of this and other properties of condensed phases. It is clear that much more needs to be done on both alcohols and other liquids and molecular solids, but the progress made has improved matters considerably as well as showing profitable directions for further work. The material

assistance from contract support in making this possible is gratefully acknowledged.

Submitted by,

Robert H. Cole
Contract Supervisor

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